The University of Chicago

THE PINACOL-PINACOLONE REARRANGEMENT: THE REARRANGEMENT OF THE TETRAMETHYLETHYLENE HALOHYDRINS

A PART OF A DISSERTATION SUBMITTED TO
THE FACULTY OF THE DIVISION OF THE
PHYSICAL SCIENCES IN CANDIDACY FOR
THE DEGREE OF DOCTOR OF PHILOSOPHY

DEPARTMENT OF CHEMISTRY
1931

By
GEORGE WASHINGTON AYERS, Jr.

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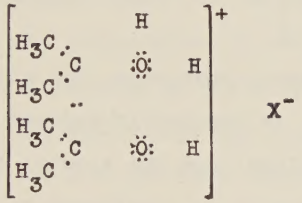
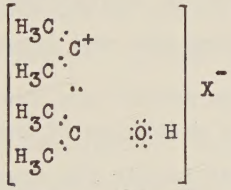
Introduction

According to the Stieglitz[1] mechanism of the pinacol-pinacolone rearrangement in which acids are the catalysts, it is assumed that an oxonium salt



is first formed, after which water is lost from this substance, leaving the nucleus



in which one of the carbon atoms possesses only three pairs of electrons. This "fault" in the molecule is the cause of the migration of one of the methyl groups with its full complement

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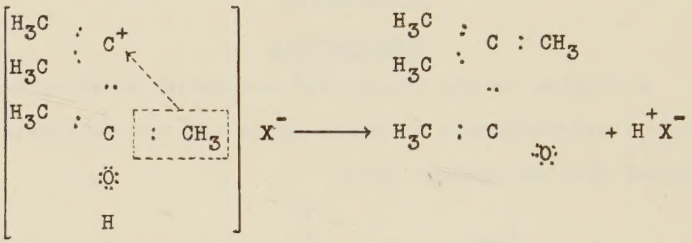
[1] Cooper, The Pinacol-Pinacolone Molecular Rearrangement, Doctor's Dissertation, University of Chicago (1930). See also Migita, Bull. Chem. Soc. Japan, 3, 308 (1928).

of electrons, that is, a negative methyl group ($:CH_3$) from the adjacent carbon atom to the positive charge of the carbon atom with a free valence:



In the rearrangement the one carbon atom, the atom to which the methyl group migrates, is completely reduced and the second carbon atom is oxidized from the alcohol to the ketone stage. The whole rearrangement is considered to be an instance of the common tendency of compounds in an intermediate stage of oxidation to revert, through migrations of electrons, toward conditions of complete reduction and complete oxidation.[1]

If the above is the true mechanism of the reaction, it might be possible to split off halide ion from the halohydrins, causing a rearrangement to the corresponding ketone. Consequently, the preparation of the chlorohydrin, bromohydrin and iodohydrin of tetramethylethylene was undertaken in order to determine whether the expected rearrangement takes place with these substances.

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[1] Jones, Am. Chem. J., 50, 441 (1913).

Results

Tetramethylethylene chlorohydrin[1] has been known for a number of years. It was prepared for the present purpose by the passage of dry hydrogen chloride into anhydrous pinacol, this method having been used by both Delacre and Detoeuf, and later modified by Mr. K. H. Adams of this laboratory. Tetramethylethylene bromohydrin, which had not previously been described in the literature, could not be prepared by the same method as was used in the preparation of the chlorohydrin because of the excessive formation of the dibromide as well as of the bromohydrin. This difficulty was overcome by the use of ether as a solvent for the anhydrous pinacol. When hydrogen bromide is passed through an ether solution of anhydrous pinacol, a mixture of the two hydrobromides of pinacol is precipitated; if the passage of gas is continued, the mixture suddenly becomes transparent. It was found that the bromohydrin was formed almost exclusively if the stream of hydrogen bromide was stopped at this point. Tetramethylethylene iodohydrin has never been reported in the literature. Both Linnemann[2] and Bouchardat[3] noted that pinacol was reduced by

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[1] Eltekow, Ber., 16, 399 (1883); J. Russ. Phys. Chem. Soc., 14, 391 (1883); Henry, Rec. trav. chim., 26, 414 (1907; Krassusky and Duda, J. prakt. Chem., [2], 77, 93 (1908); J. Russ. Phys. Chem. Soc., 39, 1070 (1907); Chem. Centr., (1908) I, 810; Couturier, Ann. chim. phys., [6], 26, 441 (1892); Delacre, Bull. soc. chim., [4], 3, 203 (1908); Ibid., [4], 1, 586 (1907); Detoeuf, Bull. soc. chim., [4], 31, 169 (1922); Adams, K. H., Doctor's Dissertation, University of Chicago (1923).

[2] Linnemann, Jahres. die Fortsch. der Chem. (1871), 422.

[3] Bouchardat, Zeit. für Chem. (1871), 699.

gaseous hydrogen iodide or by concentrated hydriodic acid. The well-known method for the preparation of iodides, consisting of the treatment of either the corresponding bromide or chloride with potassium iodide, was found to be unsatisfactory for the preparation of tetramethylethylene iodohydrin. Consequently, recourse was had to an old method used by Tiffeneau[1] in the preparation of a number of iodohydrins. Iodine and yellow mercuric oxide were shaken with a solution of the hydrocarbon in ether, ligroin, alcohol or other solvent. However, tetramethylethlene iodohydrin could not be isolated in a pure state. Only an unstable oil was formed which decomposed into pinacolone, especially under the influence of reagents such as silver nitrate, sodium thiosulfate and silver oxide.

It was found that tetramethylethylene chlorohydrin, bromohydrin and iodohydrin decomposed more or less into pinacolone when they were heated alone or treated with reagents such as silver nitrate, silver oxide and sodium thiosulfate. The chlorohydrin was the most stable substance, while the iodohydrin was so unstable that it decomposed at room temperature. Adams of this laboratory had previously found that

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[1]Tiffeneau, Ann. de chim., [8], 10, 322 (1907); Rev. gen. sci., 18, 589 (1907); Compt. rend., 145, 593 (1907); 145, 811 (1907); 147, 678 (1908); Tiffeneau and Fourneau, Bull. soc. chim. [4], 13, 971 (1913); Tiffeneau and Orekhoff, Compt. rend., 172, 387 (1921); Bull. soc. chim., 29, 809 (1921); Tiffeneau and Daudel, Compt. rend., 147, 678 (1908); Tiffeneau and Levy, Bull. soc. chim., [4], 33, 735 (1923); Tiffeneau, Orekhoff and Levy, Compt. rend., 179, 977 (1924).

there was no decomposition of the dry chlorohydrin when it was heated for six hours at 150°C. in benzene solution, but he did find decomposition to take place at 175°C. This is in accord with the well-known fact that dry tetramethylethylene chlorohydrin can be distilled[1] at 151-152°C. under atmospheric pressure. Beilstein,[2] on the other hand, noted that Krassusky[3] obtained pinacolone when the chlorohydrin was heated with or without water, but the reference cited by Beilstein did not state that the dry chlorohydrin was heated. It is easy to see how the pinacolone was formed in the presence of water by assuming hydrolysis of the chlorohydrin to pinacol and hydrochloric acid, these products always forming pinacolone when heated together. We have found that silver nitrate and silver oxide caused some rearrangement of the chlorohydrin to pinacolone, although the quantity of rearrangement product formed was very small.

Tetramethylethylene bromohydrin rearranged to pinacolone when it was heated to 100°C. The rearrangement also took place in the presence of powdered sodium bicarbonate which was added in order to remove any acid formed in the reaction which might act as a catalyst, particularly if a trace of water was present. Silver nitrate, silver oxide and sodium thiosulfate were found to be very active agents for the rearrangement of the bromohydrin, the quantity of pinacolone

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[1] Henry, Rec. trav. chim., 26, 414 (1907).
[2] Beilstein, Vol. I, p. 413, Fifth Edition (1918).
[3] Krassusky, Chem. Centr., (1902) II, 20.

formed being relatively large. Even tetramethylethylene dibromide can be rearranged to some extent by silver nitrate and silver oxide. The first step probably consists of hydrolysis to the bromohydrin which, in turn, is rearranged in the usual manner. This result with tetramethylethylene dibromide agrees with the results of previous investigators.[1]

The rearrangement of tetramethylethylene iodohydrin takes place very easily. The product formed when the iodohydrin was heated slightly on a steam bath was identified as pinacolone through formation of the corresponding semicarbazone and the determination of its melting point. The rearrangement by means of silver nitrate was practically quantitative. Even sodium thiosulfate rapidly decomposes the iodohydrin, pinacolone being formed.

In the course of the work on tetramethylethylene bromohydrin, two hydrobromides of pinacol were isolated. One was the intermediate compound postulated in the rearrangement of pinacol by hydrobromic acid, while the other consisted of two molecules of pinacol combined with one molecule of hydrogen bromide. The former hydrobromide behaved in a very interesting manner. It could not be preserved for more than a few hours in a desiccator, the substance tending to lose water and pass

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[1] Couturier, Ann. chim. phys., [6], 26, 476 (1892); Eltekow, J. Russ. Phys. Chem. Soc., 10, 220 (1878); Krassusky, J. Russ. Phys. Chem. Soc., 33, 791 (1902); Chem. Centr., (1902),I, 628.

over into the bromohydrin. In the ordinary rearrangement of pinacol to pinacolone by hydrobromic acid, it may be assumed that the small amount of pinacol hydrobromide present is in the form of oxonium ion and bromide ion. The ions are separated by water molecules and also are probably hydrated to some extent. When the positive oxonium ion splits off water, the residue remains only for an instant, after which it follows one of two possible paths: (1) one of the methyl groups from the neighboring carbon atom may migrate to the positively charged carbon atom, causing rearrangement to pinacolone, or (2) a bromide ion may add to the positively charged carbon atom, forming tetramethylethylene bromohydrin. In the case in which the oxonium ion is separated from a bromide ion by many water molecules, reaction (1) will be favored and will be the main reaction. Hence it is to be expected that pinacol hydrobromide would give pinacolone when water is split off in the presence of much water. However, when the dry pinacol hydrobromide decomposes upon standing in adesiccator at room temperature, reaction (2) will be favored. In crystalline pinacol hydrobromide the bromide ions are within atomic distances of the oxonium ions; hence when water is split from the oxonium ion, the bromide ion slips to the positively charged carbon atom and tetramethylethylene bromohydrin is formed.

Experimental

Anhydrous pinacol.- Pinacol hydrate was made by the

reduction[1] of acetone by means of magnesium amalgam in benzene. The best yields were obtained when most of the acetone was added before the reaction started.

Dehydration[2] was effected by the heating of the hydrate in a large round-bottom flask in an oil bath to 110°C., after which a vacuum was applied by means of a water-pump as long as water came off. When the suction was cut off, the oil bath was heated about 10° higher and suction was again applied. This was repeated until high-boiling liquid began to condense on the walls of the flask. At this stage the pinacol was poured into a distilling flask and distilled from an oil bath under atmospheric pressure. The fraction boiling from 170-175°C. was collected as anhydrous pinacol, the yield being about 30%. About 50% of the charge can be recovered as hydrate from the distillate obtained during the application of suction, or as partially dehydrated material distilling over before the anhydrous substance.

The almost anhydrous pinacol, as produced above, solidifies upon standing. It is water-white and can be used for most purposes without further treatment. However, absolutely anhydrous pinacol melting[3] at 38°C. and boiling at 172°C. can be made by redistillation of the above product from an oil

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[1] Org. Syntheses, Vol. V, p. 87.

[2] Adams, Doctor's Dissertation, University of Chicago, (1932).

[3] This agrees with the melting point of anhydrous pinacol as recorded in Int. Critical Tables, Vol. I, p. 204.

bath under ordinary pressure.

Tetramethylethylene chlorohydrin.- Anhydrous pinacol (100 g.) was placed in a flask immersed in a bath maintained at 45°C., Dry hydrogen chloride[1] was passed into the pinacol for six hours. The liquid was poured into 700 c.c. of ice-water and stirred vigorously during the addition in order to dissolve any unchanged pinacol and any pinacolone that had been formed. The slightly colored waxy solid which separated was kneaded several times with ice-water after which it was sucked dry on a Buchner funnel. The yield of crude tetramethylethylene chlorohydrin was 73.8 grams, which was 63.8% of the theory. (Another run gave 50% of the theoretical yield of chlorohydrin.)

Long colorless needles of pure tetramethylethylene chlorohydrin were obtained when a hot saturated solution of the crude chlorohydrin in ligroin[2] was allowed to cool. The crystals were dried in the air for a few minutes, then they were dried for one and one-half hours over phosphorus pentoxide and paraffin. The melting points of samples from different runs varied between 62°C. and 63°C.

Analysis.- Substance: 0.0551 gram; AgCl: 0.0571 gram; chlorine: found, 25.6%; calculated, 25.98%.

Tetramethylethylene chlorohydrin is a very stable

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[1]The hydrogen chloride, which was prepared by the addition of concentrated sulfuric acid to sodium chloride, was dried by passage through concentrated sulfuric acid.

[2]Ligroin boiling below 50°C.

substance at room temperature if it is perfectly dry. Even moist samples can be preserved for at least one year in a refrigerator with little or no decomposition.

The chlorohydrin is very volatile. When it was preserved in a refrigerator, some of the chlorohydrin sublimed upon the walls of the container. These crystals melted at 63°C.

The rearrangement of tetramethylethylene chlorohydrin by means of silver nitrate, silver oxide and sodium thiosulfate.- A small quantity of tetramethylethylene chlorohydrin was dissolved in ether and the resulting solution was divided into four parts.

The first portion was treated with Nessler's solution, but there was no yellow precipitate. Only the odor characteristic of tetramethylethylene oxide was noted.

The second portion was shaken with silver nitrate solution until no more precipitate formed at the interface between the two layers. Then sodium chloride solution was added in excess and the two layers filtered through a quantitative filter paper. The two clear layers of filtrate were shaken with Nessler's solution; a moderate amount of yellow precipitate, forming immediately, indicated pinacolone formation.

The third portion was shaken with a suspension of silver oxide in water and then allowed to stand for fifteen minutes. A curdy white precipitate formed very slowly. After adding a solution of sodium chloride, the mixture was filtered

and the two clear layers of filtrate were treated with Nessler's solution. Only a small amount of yellow precipitate formed, showing pinacolone formation.

The fourth portion was shaken with sodium thiosulfate solution. The upper layer was removed and shaken with Nessler's solution. A slight yellow precipitate appeared at the interface between the two liquid layers, showing pinacolone formation.

Tetramethylethylene brohomydrin.- Anhydrous pinacol (25 grams) was dissolved in 375 c.c. of anhydrous ether and a rapid stream of hydrogen bromide[1] was passed through the solution. After one minute a white precipitate formed; this settled to the bottom of the container as a faintly yellow viscous liquid. About twenty-five minutes were required for the solution to become homogeneous. At this point the clear yellow solution was washed four times with distilled water, after which it was dried over anhydrous sodium sulfate. After removal of the sodium sulfate by filtration, the ether was removed from the filtrate either by suction or by a gentle stream of air until only a pasty mass of crystals remained. This was spread upon a clay plate and left in a desiccator over calcium chloride and paraffin until the crystals were dry. The yield

[1]Hydrogen bromide was made by the drop-wise addition of bromine to a mixture of red phosphorus and 40 c.c. of water. The gas was passed through a U-tube filled with red phosphorus and glass beads. Due to the heat developed in the reaction flask, the latter was always immersed in ice-water; this prevented much bromine from passing to the U-tube.

of bromohydrin varied from 21% to 27% of the theoretical. The resulting white crystalline substance contained very little tetramethylethylene dibromide as shown by analysis. The melting point of the impure bromohydrin varied with different preparations from 66°C. to 71°C. The best results were obtained with small quantities in which the yields were small.

The crude product was recrystallized from ligroin, using the same method as was first used for obtaining the impure crystals from their solution in ether. After it had been dried in a desiccator over calcium chloride and paraffin shavings, the substance was analyzed for bromine.

Analysis.- Substance: 0.1051 gram, 0.1968 gram; AgBr: 0.1092 gram, 0.2046 gram; bromine, found: 44.22%, 44.24%; calculated: 44.15%.

The bromohydrin obtained by recrystallization from ligroin consists of a fluffy white crystalline powder having a camphoraceous odor. It melts at 70.5°C. It is very volatile at ordinary temperatures, possessing lachrymatory properties. It is very susceptible to hydrolysis; it cannot be preserved overnight at room temperature if it contains traces of water without developing brown specks and suffering a slight variation of melting point. However, perfectly dry samples of the bromohydrin can be preserved for a long time if kept in a refrigerator.

Large pure crystals of the bromohydrin, melting at 70.5°C., were obtained as a sublimate from samples of the crude

bromohydrin while they were stored in the refrigerator.

Pyrolysis of tetramethylethylene bromohydrin.- A solution of 1.12 parts of tetramethylethylene bromohydrin in 10 parts of benzene was left over anhydrous sodium sulfate in a refrigerator for 18 days. Four sealed Pyrex tubes containing this solution were then prepared. Two of the tubes were heated 6 hours at 100°C., while the remaining two tubes were heated at 150°C. for the same period. When they were opened, all of the tubes gave a yellow precipitate with Nessler's solution, as well as a red color with methyl orange solution. This indicated ketone formation. At the higher temperature there was more rearrangement since the precipitate with Nessler's solution was more voluminous than in the case where 100°C. was the temperature used.

A sample of the bromohydrin was dried 6 hours in a desiccator over calcium chloride and paraffin oil. This material decomposed immediately when heated in a small glass tube to 110°C., using a sulfuric acid bath. The experiment was repeated after the bromohydrin had been mixed with 4 parts of sodium bicarbonate. Nessler's solution again showed ketone formation.

Rearrangement of tetramethylethylene bromohydrin by means of silver nitrate, silver oxide and sodium thiosulfate.- A solution of the bromohydrin was made in anhydrous ether; it was divided into four portions. The first portion was shaken with Nessler's solution, but there was no yellow precipitate.

Only the odor of tetramethylethylene oxide was noted. The second portion was shaken with silver nitrate solution, whereupon a yellow precipitate formed immediately. After the addition of sodium chloride solution, the mixture was filtered and the two clear layers shaken with Nessler's solution. A heavy yellow precipitate formed immediately. The third portion was shaken with a suspension of silver oxide in water and then treated with sodium chloride solution. After filtration, the clear liquid layers formed a yellow precipitate after they were shaken with Nessler's solution. The fourth portion was agitated with sodium thiosulfate solution. The ether layer was decated from the milky aqueous layer and agitated with Nessler's solution. A yellow precipitate formed immediately, showing pinacolone formation.

An aqueous solution of pinacol hydrate gave no yellow precipitate with Nessler's solution after it had been agitated with silver nitrate or silver oxide and the excess of silver ion removed by precipitation with sodium chloride.

Tetramethylethylene dibromide.- Anhydrous pinacol (100 g.) was placed in a 300 c.c. Erlenmeyer flask and warmed slightly until all of the solid had melted. The flask was then immersed in ice-water[1] and hydrogen bromide[2] was passed into the colorless liquid. At first the pinacol became viscous, then it acquired a greenish-yellow color. After some

[1]The reaction liberates a large amount of heat which must be quickly absorbed or the yield of dibromide is lowered considerably. In one run in which no ice-water bath was used, the yield of dibromide was only 33.9% of the theoretical.

[2]See footnote on page 11.

time a white precipitate appeared, this precipitate becoming more granular as the absorption of hydrogen bromide proceeded. After three hours the mixture showed no further tendency to become warm while the hydrogen bromide was bubbled through it. The resulting mush consisted of pure white granular waxy crystals in a limpid brownish-red liquid. The liquid was decanted from the waxy mass of crystals which were then kneaded with ice-water until the water layer was no longer colored. The waxy mass was poured upon a Buchner funnel and washed three times with ice-water, after which the crystals were sucked dry. The yield of perfectly white crystals of the dibromide was 106.2 grams, which represented 51.3% of the theoretical. The yield from another preparation was 49.1%. This material was pure enough to use in the preparation of tetramethylethylene.

A saturated solution of the dibromide in warm ligroin[1] was prepared. When the solution became cold, pure tetramethylethylene dibromide separated out as a white granular crystalline mass. The melting point of the substance could not be determined in an open tube because of complete sublimation before the melting point was reached. One specimen melted at 184°C. in a closed tube, sublimation causing much trouble in detecting the melting point.

An analysis was made upon a purified sample which stood over phosphorus pentoxide, solid potassium hydroxide and paraf-

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[1]See footnote 2 on page 9.

fin for two hours.

Analysis.- Substance: 0.1052 gram, 0.1167 gram; AgBr: 0.1636 gram, 0.1818 gram; bromine: found, 66.19%, 66.29%; calculated, 65.55%.

The effect of silver nitrate and silver oxide upon tetramethylethylene dibromide.- A solution of the dibromide in ether was divided into three parts. The first portion was treated with Nessler's solution, but there was no precipitate. The second portion was shaken with a solution of silver nitrate, but precipitation occurred less readily than in the case of the bromohydrin. After the addition of sodium chloride solution, the mixture was filtered and the filtrate treated with Nessler's solution. There was a distinct yellow precipitate. The third portion was shaken with a suspension of silver oxide in water and allowed to stand for two hours. Then a solution of sodium chloride was added and the mixture filtered. The filtrate was treated with Nessler's solution, but only a slight precipitate formed.

Tetramethylethylene.-[1] Tetramethylethylene dibromide (100 g.) was weighed into a liter flask. Then 500 c.c. of glacial acetic acid was added and the mixture shaken while the flask was cooled in ice-water. When the temperature of the mixture reached 16°C., fifty grams of zinc dust was added in very small portions, the flask being continuously shaken. The temperature of the mixture was never allowed to exceed 20°C.

[1] Thiele, Ber., 27, 455 (1894).

The reaction between the zinc dust and the dibromide was almost instantaneous. After all of the zinc dust had been added, the contents of the flask were allowed to come to room temperature. The mixture was then diluted with two liters of cold water. After agitation the mixture was allowed to stand for one and one-half hours. The lower aqueous layer was then removed and the crude tetramethylethylene washed twice with cold water. The crude hydrocarbon weighed 26.5 grams. (Another run gave 25 grams.)

The crude hydrocarbon was placed in a 500 c.c. distilling flask along with 100 c.c. of water containing about half a gram of potassium hydroxide. Steam was passed into the distilling flask while the latter was heated gently with a flame. When the temperature of the mixture reached 75°C., the hydrocarbon distilled over almost completely. Only the material which distilled within the first fifteen minutes was collected. This was separated from the water layer and dried over anhydrous sodium sulfate. The yield of the colorless liquid was 21.1 grams. (Another run gave 18.8 grams.) The hydrocarbon had an odor similar to that of pine oil. The specific gravity of the substance ranged from .7217 to .7262 at 25°C. for different runs.

Thirty-seven grams of the semi-purified hydrocarbon (specific gravity 0.7240 at 25°C.) was weighed into a flask and fractionated. A Hempel column which was lagged with asbestos and filled with glass beads was used in the factiona-

tion. The characteristics of the various fractions are shown in the following table:

Table I

Fractionation of Semi-purified Tetramethylethylene

	Fraction I	Fraction II	Fraction III	Residue
Boiling Range (753 mm.)	71.9-72.6°C.	72.6°C.-72.9°C.	72.9°C.	____
Specific Gravity at 25°C.	0.7016	0.7028	____	____
Refractive Index at 20°C. (N_D)	1.4127	1.4127	____	____
Refractive Index at 25°C. (N_D)	1.4099	1.4101	____	____
Odor	Reminiscent of pine and yeast	Stronger pine odor; also odor like that of yeast	Stronger pine odor	Strong pine odor
Color	Colorless	Colorless	Colorless	Brown
Yield	15.4 g.	13.4 g.	1.1 g.	2.8 g.

Fractions I and II are pure tetramethylethylene. The yield was 28.8 grams, which represents 83.6% of the theoretical.

Iodine number of tetramethylethylene by thw Wijs method.- One cubic centimeter of hydrocarbon was pipetted into a 50 c.c. volumetric flask almost filled with carbon tetrachloride. After the contents were mixed, the flasks were filled to the mark with carbon tetrachloride. Ten cubic centi-

meters of this solution was pipetted into an iodine flask, then 50 c.c. of Wijs solution[1] was added and the flasks allowed to stand for one hour in darkness. Then 20 c.c. of fifteen per cent potassium iodide solution was added. This was followed by 50 c.c. of water, after which the iodine was titrated with standard sodium thiosulfate solution. A black determination was run with pure carbon tetrachloride. The results are given in the following table:

Table II

Iodine Number of Tetramethylethylene

Temperature at Which Experiment Was Performed	Fraction I	Fraction II
Room Temperature	349.7[2]	359.7
0°C.	326.5	333.8
-4°C.	325.2	329.8
Theoretical	302.0	302.0

Tetramethylethylene iodohydrin.- Tetramethylethylene (2 g.) was dissolved in 10 c.c. of alcohol in a small flask. Then 6 grams of iodine was added and the flask cooled in ice-water during the addition of 2.5 grams of yellow mercuric oxide. A red precipitate of mercuric iodide settled to the bottom of the flask. A small amount of the alcoholic solution

[1] Wijs solution was made by the solution of 13.2 grams of iodine in one liter of glacial acetic acid, after which chlorine was passed into the solution until most of the iodine was converted into iodine chloride. An excess of iodine rather than of chlorine is essential.

[2] All results are averages of two or more values.

was filtered after solution was effected. Only a slight cloudiness and yellow color formed when Nessler's solution was added to the filtrate. This showed that only a trace of pinacolone was present. The remainder of the original alcoholic solution was poured into a large volume of ice-water. A camphoraceous odor was noted at the same time that a red oil settled to the bottom of the container. After the red oil had been washed several times by decantation, it was divided into two portions. The first portion was agitated with dilute sodium thiosulfate solution in order to remove the excess of iodine, but this treatment was too severe because the oil decomposed very readily. It was found to be impossible to remove the free iodine without destroying the oil at the same time. After the treatment with sodium thiosulfate, the solution was found to contain free acid and much pinacolone (voluminous yellow precipitate with Nessler's solution). The second portion of the red oil was dissolved in ether and agitated with silver nitrate solution. The precipitate was filtered off and the filtrate shaken with sodium chloride solution. After a second filtration, the filtrate gave a voluminous yellow precipitate with Nessler's solution.

Since the unstable oil mentioned above might have been a mixture of the iodohydrin and ethyl iodohydrin[1] of tetramethylethylene, other solvents than alcohol were used in the

[1] Tiffeneau and Orekhoff, Bull. soc. chim., 29, 809 (1921), made the methyl iodohydrin of dimethylstyrene when a similar procedure was followed, using absolute methyl alcohol as the solvent.

preparation. When a ligroin boiling below 50° C. was used as the solvent, an unstable oil was formed which liberated iodine and which had a camphoraceous odor. Much of the oil was decomposed during the removal of the ligroin. Pinacolone was definitely identified among the decomposition products from the melting point of the semicarbazone.

When ether was used as the solvent in the preparation of the iodohydrin the following procedure was used: Nine grams of hydrocarbon was dissolved in 50 c.c. of moist ether[1] and a solution of twenty-five grams of iodine in 150 c.c. of moist ether was added to this solution. Ten grams of water and ten grams of yellow mercuric oxide were then added along with a few pieces of ice. Finally, the mixture was shaken for thirty minutes, after which the ether layer was agitated with just enough dilute sodium thiosulfate solution to remove the free iodine. After the ether layer was washed three times with water, no more iodide ion was present in the washings. The ether solution was divided into three portions. The first portion was evaporated by means of a current of air. While crystals of pinacolone separated from the cold solution along with a small amount of unstable oil. This material formed a semicarbazone melting at 148° C. The second portion of the ether solution was agitated with silver nitrate solution, fil-

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[1]The ether was washed six times with distilled water in order to remove any alcohol which was present.

tered and then shaken with sodium chloride solution. After a second filtration, the ether solution was evaporated leaving pinacolone. The semicarbazone[1] prepared from this substance melted at 155°C. The third portion of the ether solution was found to react very slowly with yellow mercuric oxide to form red mercuric iodide and pinacolone.

It was noted that no yellow mercuric oxide was necessary in the preparation of the iodohydrin by the ether method, but the yield was much smaller than when the yellow mercuric oxide was used.

Molecular weight of anhydrous pinacol in benzene.- Results by the freezing point method indicated that anydrous pinacol is dimolecular in benzene solution:

	Weight of Sample		Lowering	Molecular Weight
	Pinacol	Benzene[2]	°C.	(Found)
First Trial	24.138	526.4	.960	245
Second Trial	23.201	554.4	.927	231

The calculated molecular weight of $(C_6H_{14}O_2)_2$ is 236.

Di-pinacol hydrobromide $[(C_6H_{14}O_2)_2H]$ Br.- Gaseous hydrogen bromide was passed through a solution of 5 grams of anhydrous pinacol in 125 c.c. of ligroin (distilling below

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[1] Pinacolone semicarbazone melted at 157°C. according to Carlinfanti, Gazz. Chim. Ital., 27, II, 387.

[2] Merck's Reagent Quality benzene was used for this work.

50°C.) until there was no more precipitation. The sticky white mass was washed four times with ligroin after which it was smeared on a clay plate and left overnight in a desiccator over sulfuric acid and paraffin. The next day the material was titrated with standard potassium hydroxide solution and phenolphthalein indicator. The results are expressed under "A" in Table III.

A solution of 5 grams of anhydrous pinacol in 75 c.c. of carbon tetrachloride was treated with gaseous hydrogen bromide. A yellow oily layer formed on the carbon tetrachloride after the primary cloudiness. Upon continued absorption of hydrogen bromide the oily layer became more and more viscous, finally becoming mealy. After the crystals were washed four times with carbon tetrachloride, they were smeared on a clay plate and placed overnight in a desiccator over calcium chloride and paraffin. The analysis is given under "B" in Table III.

Table III

	"A"	"B"
Sample	.2900 g.	.4489 g.
c.c. .4363 N-KOH used	2.08 c.c.	3.23 c.c.
H Br (found)	25.3%	25.4%
H Br calculated for $\left[(C_6H_{14}O_2)_2 \cdot H\right]Br$	25.5%	25.5%

Di-pinacol hydrobromide has a granular appearance when first precipitated; after standing in a desiccator it

forms large well-defined crystals. The substance is fairly stable at room temperature in a dry atmosphere; if it is left exposed to the air, it rapidly absorbs moisture, forming a solution of pinacol and hydrobromic acid. One specimen was preserved for two weeks in a desiccator, analyses showing that practically no decomposition occurred during that time. The melting point was found to be 52-54°C. The substance dissolves instantly in water.

Pinacol hydrobromide, $[(C_6H_{14}O_2.H\ ]\ Br)$.- This was prepared by the same method that Harries[1] used for the hydrochloride. Anhydrous pinacol (5 grams) was dissolved in 8 volumes of chloroform. The solution was cooled in ice-water, after which gaseous hydrogen bromide was passed into the cold solution. No precipitate formed for some time, then suddenly the whole solution became solid. Hydrogen bromide was still passed through the mixture for a minute longer, after which the material was poured on a Buchner funnel. After one wash with chloroform, the crystals were slapped on a clay plate and placed in a desiccator over calcium bromide and paraffin.

Analysis.- Sample: 0.8919 gram; 46.78 c.c. of .09632 Normal potassium hydroxide with phenolphthalein as indicator; HBr, found: 40.88%; HBr, calculated: 40.68%.

Pinacol hydrobromide is a colorless crystalline substance which fumes in moist air and which is soluble in water.

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[1] Harries, Ann., 383, 183 (1911).

It is rather unstable at room temperature. A sample of the hydrobromide was kept in a desiccator over calcium bromide and paraffin for two days. At the end of that time there was only a trace of solid substance left on the clay plate; it showed only 35.9% hydrogen bromide by titration. However, much bromohydrin was present as was noted by the odor. Hydrogen bromide was not present. This indicated that the hydrobromide slowly formed tetramethylethylene bromohydrin at room temperature.

Behavior of a mixture of the hydrobromides.- When a stream of hydrogen bromide was led into an ether solution of anhydrous pinacol, a mixture of both hydrobromides was ordinarily obtained. When this material was left in a desiccator over calcium bromide and paraffin for several days, the true hydrobromide formed the bromohydrin which sublimed out of the mixture, leaving the di-pinacol hydrobromide. This latter substance is very stable in a dry atmosphere and does not spontaneously form the bromohydrin.

Summary

1. Tetramethylethylene bromohydrin was prepared for the first time by the passage of hydrogen bromide into an ether solution of anhydrous pinacol until the precipitate first formed was just dissolved.

2. Tetramethylethylene iodohydrin was prepared as an unstable oil by the agitation of iodine and yellow mercuric oxide with a solution of tetramethylethylene in various solvents.

3. Two hydrobromides of pinacol were formed by the passage of hydrogen bromide into solutions of pinacol in various solvents.

4. Tetramethylethylene chlorohydrin, bromohydrin, and iodohydrin were decomposed into pinacolone by heat and by agitation with reagents such as silver nitrate, silver oxide and sodium thiosulfate. The chlorohydrin was the most stable, while the iodohydrin was the least stable substance. The latter decomposed at room temperature.

5. Anhydrous pinacol was found to be dimolecular in benzene at the freezing point of the latter substance.

6. Tetramethylethylene was prepared in very pure condition by Thiele's method.

7. The results given in this paper verify the Stieglitz mechanism of the pinacol-pinacolone rearrangement.